Solubility of 1-Hexadecanol and Palmitic Acid in Supercritical Carbon Dioxide

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By use of a continuous flow facility, vapor-phase compositions in supercritical carbon dioxide at 318, 328, and 338 K have been measured for 1-hexadecanol ($CH_3(CH_2)_{14}CH_2OH$) and palmitic acid ($CH_3(CH_2)_{14}COOH$) for pressures of 140-416 and 140-575 bar, respectively. For the isothermal measurements, the mole fraction compositions related with the corresponding reduced density of the supercritical solvent as follows: $\log y_2 = A + B\rho_{R_1}$. The temperature-dependent parameters A and B were capable of producing compositions with average deviations of 3.4% (18 points) for the 1-hexadecanol-carbon dioxide and 9.7% (19 points) for the palmitic acid-carbon dioxide systems. The coupling of the Flory-Huggins theory with the three-dimensional solubility parameter of the solvent predicts, through the introduction of a single interaction parameter, the compositions with average deviations of 11.4% (18 points) for the 1-hexadecanol and 20.2% (19 points) for the palmitic acid binary systems.

Limited fundamental studies on the solubilities of heavy cut detergent range alcohols (16 through 18 carbon atoms) and their related fatty acids are presented in the literature. Giddings et al. (*1*) and Czubryt et al. (*2*) accounted for the solubility of 1-octadecanol and stearic acid in dense supercritical carbon dioxide at 313 K using a high-pressure gas chromatographic facility. Using this approach, these investigators measured the threshold pressures and solubility enhancement of these compounds for pressures ranging from 300 to 2000 bar. Through these means, they were able to detect the maximum solubility of these solutes to occur at a pressure around 300 bar.

The present study was initiated to investigate quantitatively the solubility of 1-hexadecanol [$CH_3(CH_2)_{14}CH_2OH$] and its corresponding palmitic acid [$CH_3(CH_2)_{14}COOH$] in supercritical carbon dioxide at temperatures of 318, 328, and 338 K. The ability to obtain these compounds in their pure form is of significant interest because of their extensive use in the cosmetic, pharmaceutical, and surfactant industries. For example, these compounds are extensively used in cosmetics as soothing additives, intermediates for perfumes, and flavor components and as bases for creams and ointments.

Experimental Studies

Both the 1-hexadecanol and the palmitic acid were supplied by the Eastman Kodak Co. Each was of reagent grade with a claimed purity of 95%. For 1-hexadecanol, its melting point range was claimed to be 2 °C in the vicinity of 50 °C. The carbon dioxide was supplied by the Linde Division of Union Carbide and was of bone dry grade with a minimum purity of 99.8%.

The experimental facility was of the continuous flow type and is presented schematically in Figure 1. The solid solute to be dissolved was confined within a saturator which was totally submerged in a constant temperature bath. The saturator consisted of a ready made stainless steel pipe nipple (20.32 cm in length and 1.31 cm in inside diameter) with reducer-adapter couplings at each end. These components were standard parts supplied by Autoclave Engineers Inc. The assembled unit was capable of withstanding pressures up to 700 bar and 311 K and was tightly packed with alternate layers of the ground solute (5-7 layers) and glass wool. Roughly 12-13 g of solute was charged inside the saturator before initiating a run. This saturator was attached to a preheating coil and the assembly of both was submerged into a constant temperature water circulating bath. The temperature inside the water bath was regulated within ±0.1 °C through the use of heating elements and a proportional type temperature controller (Barber-Colman, Model 560) using a J-type thermocouple. The actual temperature of the bath was continuously checked with a mercury thermometer. Carbon dioxide was supplied from a gas cylinder and was directed to a diaphragm air-driven compressor after passing through a high pressure T-type filter (supplied by the Linde Division of Union Carbide). This filter had a filtration rating of 0.6 μm at a 99.9% efficiency. The diaphragm compressor (Model 746-14025-1) was supplied by Newport Scientific Inc. and was rated for a maximum operating pressure of 700 bar. The mechanical design of this compressor prevents the contamination of the compressed gas with foreign materials. After compression, the carbon dioxide was introduced into a surge vessel (volume = 1000 cm^3) to dampen the fluctuations generated by the operation of the compressor. Immediately after the compressor, all high-pressure lines were heated with electrical tape to prevent condensation of the carbon dioxide.

In order to maintain a constant pressure within the system, a hand adjustable back pressure regulator with a stated accuracy of ±1% of the relief pressure range (manufactured by Tescom Co. Series 26-1700) was employed. During the operation of the system, it was found that best performance could be achieved by keeping this regulator always slightly open, after reaching the desired pressure, and thus allowing the flow of 200-300 cm^3 (STP)/min to pass through. This approach permitted better pressure control of the system with fluctuations within ±0.5-2.0 bar. Also to prevent clogging with solid carbon dioxide, this regulator was wrapped with electrical heating tape and was heated constantly to 323-333 K. The controlled pressure range for this back pressure regulator was 20-700 bar. Two modes of operation were employed in handling the excess gas that discharged through this back pressure regulator, one by relieving the gas directly to the atmosphere (valve V2 open and valve V1 closed) and the other when the excess gas was recycled back into the system (valve V1 open and valve V2 closed).

Pressure measurements for the system were made using two mercury-loaded high-pressure Heise gauges having pressure ranges of 0-150 and 0-1000 bar. These gauges were calibrated with a dead weight gauge (Mansfield and Green Co., Model 150, Serial 4350) which was connected to the system through an oil-mercury separator.

A modified version of a micrometering valve supplied by Autocalve Engineers Inc. (Part No. 60VR MM 4882) provided a fine adjustment of the output flow from the saturator which contained the dissolved solute. Through this valve, the high pressure in the system was reduced to atmospheric pressure where the solute commenced to separate from the solvent. The basic features of this micrometering valve that permitted these precise adjustments were a finely tapered stem, a fine operating thread, and an orifice size of 1.57 mm. An electrical

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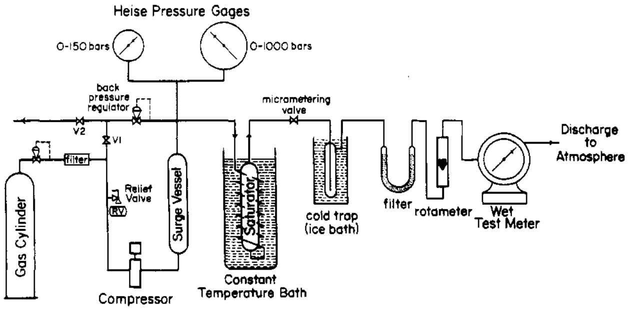

Figure 1. Schematic diagram of experimental apparatus.

heating tape prevented clogging of the valve with the precipitated solute by heating this valve 25–35 °C above the corresponding melting point of the solute. After initial adjustments in the course of a run, it was possible to achieve a steady flow of 55–65 cm^3 (STP)/min.

The collection of the solute sample was accomplished in the following manner. After the desired pressure was achieved, the system was allowed to stabilize for approximately 20–30 min. Then, the micrometering valve was slightly opened and the output flow was established through the rotameter. To assure that equilibrium within the saturator had been achieved, measurements were taken at different flow rates ranging from 40 to 200 cm^3 (STP)/min. In this manner, it was established that flow rates at 55–62 cm^3 (STP)/min yielded the most consistent stable results. The cold trap was attached directly to the micrometering valve with a high-pressure connection and was submerged in an ice bath.

The sampling approach consisted of weighing the trap before and after a run to account for the solute precipitated within it. This trap was packed with glass wool. The amount of solute collected ranged between 0.06 and 0.40 g. The U-tube was also packed with glass wool and was installed immediately after the cold trap. It was established that more than 99.9% of the solute was collected in this cold trap.

This experimental facility was tested with the naphthalene–carbon dioxide system at 318 and 328 K and pressures of 96–330 bar. These results were compared with the experimental measurements reported by Tsekhanskaya et al. (*3*) and were within 5% in agreement.

Treatment of Experimental Measurements

The measured solubilities of 1-hexadecanol and palmitic acid in supercritical carbon dioxide at 318, 328, and 338 K are presented in Table I and Table II, respectively. Since it has been established by Giddings et al. (*1*) that the solvation power of a solvent is directly linked with its corresponding density, this suggests the possible existence of a relationship between the density of the fluid and the mole fraction of the solute dissolved in the fluid phase. Upon plotting on semilogarithmic coordinates y_2, the mole fraction of the solute, versus ρ_{R_1}, the reduced density of the pure solvent, it was found that linear relationships result for each isotherm of the systems investigated. This behavior suggests this dependence to be of the form

$$\log y_2 = A + B\rho_{R_1} \tag{1}$$

The temperature dependence of the parameters A and B was found to be as follows:

1-hexadecanol–carbon dioxide system

$$A = -0.0078T - 2.115 \tag{2}$$

$$B = 0.01683T - 3.9567 \tag{3}$$

palmitic acid–carbon dioxide system

$$A = 0.00975T - 2.64312 \tag{4}$$

$$B = 0.02261T - 5.31583 \tag{5}$$

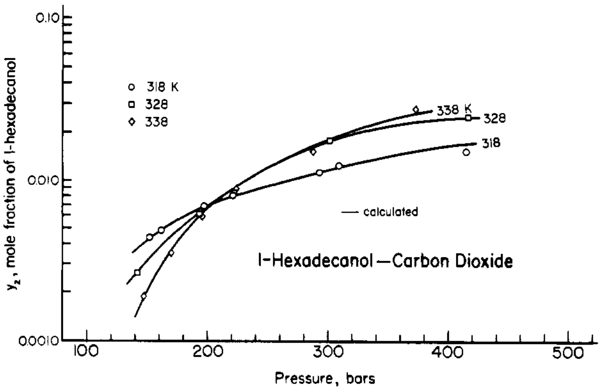

Figure 2. Experimental and calculated solubilities of 1-hexadecanol in supercritical carbon dioxide.

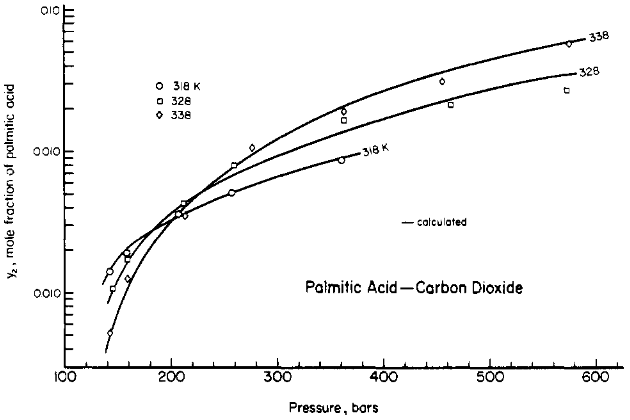

Figure 3. Experimental and calculated solubilities of palmitic acid in supercritical carbon dioxide.

These parameters have been applied for the calculation of vapor-phase compositions for 1-hexadecanol and palmitic acid and the results are presented in Tables I and II. When these calculated values are compared with corresponding experimental measurements, they produce overall average deviations of 3.4% (18 points) for the 1-hexadecanol–carbon dioxide system and 9.7% (19 points) for the palmitic acid–carbon dioxide system. The reduced densities for carbon dioxide were obtained from the work of Kennedy and Thodos (*4*). Equations 2–5 result from the direct experimental measurements and, as such, they are specific to the systems investigated. The results of the application of eq 1 are shown for these two binary systems as the solid curves of Figures 2 and 3.

Following another argument in which the supercritical fluid is treated as an expanded liquid and the solid solute as a subcooled liquid, the mole fraction of the heavy component in the fluid phase can be calculated by using the following approach. For these supercritical conditions, it is possible to show that the mole fraction of the solute in the fluid phase can be expressed as

$$y_2 = \frac{1}{\gamma_2^{\infty}} \frac{f_2^{0s}}{f_2^{0l}} \tag{6}$$

where γ_2^{∞} is the activity coefficient of the solute at infinite dilution in the fluid phase and the ratio, f_2^{0s}/f_2^{0l}, represents the involvement of fugacities of the pure solute in the solid phase, f_2^{0s}, and that of the fluid phase, f_2^{0l}, which is treated as an expanded liquid. At some experimental conditions, the solute can exist as a liquid under the influence of pressure and definitely for temperatures above the melting point of the solute. When the solute is liquefied, the ratio f_2^{0s}/f_2^{0l} becomes unity.

Table I. Experimental Data and Calculated Values for the 1-Hexadecanol-Carbon Dioxide System

	10^2y_2, mole fraction			abs dev, %		solvent properties		β_{12}	
P, bar	exptl	eq 1	eq 6	eq 1	eq 6	ρ_R	δ	actual	pred
T = 318 K (45 °C)									
152.1	0.437	0.448	0.452	2.4	3.52	1.61	6.46	16.00	16.09
161.8	0.486	0.493	0.508	1.4	4.59	1.64	6.56	15.79	15.90
197.1	0.697	0.680	0.792	2.5	13.6	1.74	6.98	14.93	15.21
221.0	0.804	0.773	0.916	3.9	14.0	1.78	7.14	14.70	14.99
292.5	1.13	1.10	1.27	2.6	12.6	1.89	7.58	14.23	14.49
309.5	1.24	1.21	1.37	2.3	10.8	1.92	7.72	14.12	14.35
415.1	1.53	1.67	1.60	9.2	4.52	2.02	8.12	13.92	14.02
				3.5	9.09				
T = 328 K (55 °C)									
141.8	0.267	0.264	0.225	1.1	15.6	1.34	5.38	20.85	20.48
192.6	0.621	0.627	0.664	0.9	6.91	1.58	6.34	17.37	17.53
220.3	0.826	0.836	0.920	1.2	11.3	1.66	6.66	16.62	16.86
301.1	1.81	1.85	1.80	1.9	0.75	1.88	7.54	15.60	15.59
415.9	2.53	2.46	2.06	2.7	18.7	1.96	7.86	15.71	15.27
				1.6	10.6				
T = 338 K (65 °C)									
147.1	0.190	0.181	0.194	4.8	2.16	1.16	4.63	25.81	25.87
169.8	0.352	0.371	0.330	5.4	6.29	1.34	5.38	21.97	21.83
195.7	0.607	0.648	0.552	6.8	9.03	1.48	5.92	20.04	19.84
223.2	0.898	0.892	0.757	0.7	15.7	1.56	6.24	19.28	18.91
287.0	1.55	1.62	1.28	4.6	17.4	1.71	6.86	18.02	17.60
373.0	2.81	2.62	1.75	6.9	37.7	1.83	7.34	17.91	16.86
				4.9	14.7				

Table II. Experimental Data and Calculated Values for the Palmitic Acid-Carbon Dioxide System

	10^2y_2, mole fraction			av dev, %		solvent properties		β_{12}	
P, bar	exptl	eq 1	eq 6	eq 1	eq 6	ρ_R	δ	actual	pred
T = 318 K (45 °C)									
142.1	0.142	0.145	0.111	2.1	21.8	1.55	6.22	10.98	10.46
158.2	0.193	0.205	0.197	6.1	20.9	1.63	6.54	10.27	10.32
206.6	0.360	0.344	0.403	4.5	11.8	1.75	7.02	9.93	10.18
257.1	0.519	0.507	0.609	2.4	17.3	1.84	7.38	9.76	10.10
360.6	0.870	0.888	0.910	2.1	4.5	1.97	7.90	9.94	10.04
				3.4	15.3				
T = 328 K (55 °C)									
144.1	0.109	0.099	0.073	9.5	33.5	1.35	5.42	10.76	9.88
158.2	0.174	0.168	0.165	3.5	5.17	1.46	5.84	9.43	9.32
211.2	0.431	0.421	0.617	2.3	43.3	1.65	6.62	7.96	8.74
259.9	0.813	0.683	1.04	16.0	28.5	1.75	7.02	8.03	8.58
362.1	1.67	1.34	1.78	19.5	6.5	1.89	7.58	8.30	8.44
463.9	2.15	2.29	2.26	6.4	4.9	2.00	8.02	8.26	8.37
573.5	2.77	3.37	2.41	21.6	12.9	2.08	8.32	8.63	8.34
				11.3	19.2				
T = 338 K (65 °C)									
142.5	0.052	0.044	0.05	15.4	3.7	1.11	4.45	11.96	11.88
159.0	0.129	0.109	0.114	15.2	11.4	1.28	5.11	9.28	9.03
213.8	0.351	0.418	0.585	19.0	66.6	1.53	6.14	5.94	7.07
277.0	1.09	0.93	1.34	14.4	22.6	1.68	6.74	6.12	6.58
362.7	1.91	2.08	2.46	9.0	28.7	1.83	7.34	5.74	6.31
454.9	3.17	3.56	3.19	12.2	0.6	1.93	7.74	6.18	6.20
574.8	5.96	5.76	3.64	3.3	39.0	2.02	8.12	7.22	6.13
				12.6	24.7				

The activity coefficient, γ_2^{∞}, can be obtained from the definition of Hansen's three-dimensional solubility parameter (*5*)

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (7)$$

where δ_t is the total solubility parameter and δ_d, δ_p, and δ_h are the corresponding dispersion, polar, and hydrogen-bonding contributions. This definition for the solubility parameter, together with the Flory–Huggins theory, as shown by Kramer (*6*), results in the final expression

$$\ln \gamma_2^{\infty} = \frac{v_2}{RT}[(\delta_{d_1} - \delta_{d_2})^2 + \tau_2^2 - \beta_{12}] + 1 + \frac{v_2}{v_1} + \ln \frac{v_2}{v_1} \qquad (8)$$

where $\tau^2 = \delta_p^2 + \delta_h^2$. The binary interaction parameter, β_{12}, accounts for the binary molecular interaction between the solvent and solute. In eq 8, v_1 is the molar volume of the solvent and v_2 is the molar volume of the subcooled solute obtained by the extrapolation of its corresponding liquid molar volume. The basic physical properties of 1-hexadecanol and palmitic acid at different temperatures needed for eq 8 are presented in Table III. In this table are also included the values for 298 K because the dispersion contribution for these solutes, δ_{d_2}, was established from the group molar attraction contribution technique given by Koenhen and Smolders (*11*) at this temperature. Using the suggestion given by Hansen and Beerbower (*12*), the temperature dependence for this contri-

Table III. Solubility Parameters at Different Temperatures for 1-Hexadecanol and Palmitic Acid[a]

	1-hexadecanol (T_m = 322.30 K)				palmitic acid (T_m = 335.66 K)			
	298 K	318 K	328 K	338 K	298 K	318 K	328 K	338 K
ΔH^{vap}, kcal/mol	27.95	26.39	25.68	24.97	27.85	26.33	25.62	24.91
v_2, cm^3/mol	290.18	295.12	297.66	300.28	293.28	298.22	300.76	303.38
δ_{t_2}, (cal/cm^3)$^{1/2}$	9.710	9.342	9.170	8.996	9.648	9.282	9.112	8.939
δ_{d_2}, (cal/cm^3)$^{1/2}$	8.210	8.033	7.946	7.860	7.995	7.823	7.738	7.654
τ, (cal/cm^3)$^{1/2}$	5.185	5.454	5.580	5.071	5.400	4.996	4.817	4.617
f_2^{0s}/f_2^{0l}		0.7527	1.000	1.000		0.3469	0.6439	1.000

[a] ΔH^{vap} and v_2 obtained from the extrapolation of values given by Smith (*7*) and Barton (*10*). ΔH^{fus} needed for the calculation of f_2^{0s}/f_2^{0l}, values were obtained from Mosselman et al. (*8*). For 1-hexadecanol, T_m = 322.30 K obtained from Mosselman et al. (*8*). For palmitic acid, T_m = 335.66 K obtained from Shaake et al. (*9*).

bution was obtained from the relationship given by Hildebrand and Scott (*13*)

$$\mathrm{d}\ln \delta_d/\mathrm{d}T = -1.25\alpha \tag{9}$$

where α is the coefficient of thermal expansion and was calculated to be 0.000 870 1 K^{-1} for 1-hexadecanol. This value was also taken to apply for palmitic acid.

The total solubility parameter, δ_t, for carbon dioxide was calculated by using the classical approach presented by Hildebrand and Scott (*13*) as

$$\delta_{t_2} = \left(\frac{\Delta H_2^{vap} - RT}{V_2}\right)^{1/2} \tag{10}$$

Following this logic, the combined polar and hydrogen bonding contribution was obtained as

$$\tau = (\delta_{t_2}^{\ 2} - \delta_{d_2}^{\ 2})^{1/2} \tag{11}$$

If it is assumed that $\delta_{t_1} \approx \delta_{d_1}$, the solubility parameter for the solvent can be calculated, as a first order of approximation, from the relationship proposed by Giddings et al. (*1*)

$$\delta_{d_1} = 1.25 P_c^{\ 1/2}\, \rho_{R_1}/\rho_{Rl_1} \tag{12}$$

where δ_{d_1} is in units of (cal/cm^3)$^{1/2}$, P_c is the critical pressure in atmospheres, ρ_{R_1} is the reduced density, and ρ_{Rl_1} is the limiting reduced density of the liquid state of the solvent, taken normally as 2.66.

In order to use eq 8, β_{12} must be available. This parameter represents the interaction between molecules of the solute and solvent existing in the fluid phase. Values for this parameter were obtained from the experimental data and are presented in Tables I and II. These values exhibited a strong dependence on the solubility parameter of the pure solvent and a weak dependence on temperature. In equation form, this parameter has been correlated to yield the expressions for the 1-hexadecanol–carbon dioxide system as

$$\beta_{12} = \frac{2300}{e^{0.00445T + 1200/T}}\left[1 + \frac{12476}{e^{0.6038\delta_{d1}}}\right] \tag{13a}$$

and for the palmitic acid–carbon dioxide system as

$$\beta_{12} = 14.2 - 4.50 \times 10^{-27}\left[1 - \frac{61.62}{e^{\delta_{d1}}}\right]T^{10.78} \tag{13b}$$

Predicted values for β_{12} by use of eq 13a and eq 13b are given in Tables I and II. The fluid-phase compositions resulting from these values calculated with eq 6 are also presented in these tables together with their corresponding average deviations. The overall average deviation was found to be 11.4% (18 points) for the 1-hexadecanol–carbon dioxide system, and 20.2% (19 points) for the palmitic acid–carbon dioxide system.

Conclusions

The experimental measurements for the solubility of 1-hexadecanol and palmitic acid in supercritical carbon dioxide have been successfully modeled by using two different semiempirical approaches. Both methods yield results that are consistent for the temperatures investigated. Unfortunately the solids investigated were not of the desired purity and each could contain up to 5% impurities. Therefore, the obtained experimental solubilities could differ somewhat from corresponding values resulting from constituents of higher purity. However, the experimental procedure employed in the present study was designed to minimize the effect of these impurities by rejecting the initial samples corresponding to each experimental point. Investigations of this type involving long-chain alcohols and their corresponding acids offer a means for their purification which can have a commercial impact for obtaining compounds which are very expensive in their pure form (*14*).

Both modeling procedures employed produced results that are compatible and show an improvement over corresponding approaches using an equation of state procedure which according to Haselow et al. (*15*) results in overall deviations of roughly 40%.

Glossary

A, B	parameters, eq 1
f	fugacity, bar
ΔH	molar heat, cal/mol
P	pressure, bar
R	gas constant, 1.9872 cal/(mol K)
T	temperature, K
v	molar volume, cm^3/mol
y	mole fraction of component in vapor phase

Greek Letters

α	coefficient of thermal expansion, K^{-1}
β	interaction parameter
γ	activity coefficient
δ	solubility parameter, (cal/cm^3)$^{1/2}$
ρ	density, g/cm^3
τ	$= (\delta_p^{\ 2} + \delta_h^{\ 2})^{1/2}$

Subscripts

1	solvent
2	solute
c	critical
d	dispersion
h	hydrogen bonding
l	liquid phase
m	melting point
p	polar
R	reduced
t	total

Superscripts

fus	fusion
l	liquid

0	pure component
s	solid
vap	vaporization
∞	infinite

Registry No. CO_2, 124-38-9; $CH_3(CH_2)_{14}COOH$, 57-10-3; $CH_3(CH_2)_{14}CH_2OH$, 36653-82-4.

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Viscosity and Density of Some Lower Alkyl Chlorides and Bromides

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A high-pressure capillary viscometer, used previously to measure the viscosity of methyl chloride [*J. Chem. Eng. Data* 1984, *29*, 163], was rebuilt to eliminate the first-order dependence of the measured viscosity on the value assumed for the density of the fluid being investigated. At the same time, the system was arranged so that part of the apparatus could be used to measure density by a volumetric displacement technique. Viscosity and density were measured for ethyl chloride, 1-chloropropane, 1-chlorobutane, methyl bromide, ethyl bromide, and 1-bromopropane. The temperature and pressure ranges of the experiments were 20–150 °C and 0.27–6.99 MPa, respectively. The accuracy of the viscosity measurements was estimated to be ±1% and of the density measurements, ±0.2%.

Introduction

A previous paper described the construction and calibration of a high-pressure capillary viscometer and its use to measure the viscosity of liquid-phase methyl chloride in the temperature range from 20 to 150 °C (*1*). The viscometer was a device of moderate precision, calibrated with respect to the known viscosity of helium at 25 °C.

Volumetric flow in the original device was established by piston displacement of the working fluid at a temperature of 25 °C. In order to derive the viscosity from the observed data, it was necessary to know the change in density of the fluid between pump temperature and the temperature of the viscosity measurement. For many compounds these data are not available in the temperature ranges of interest.

The viscometer was rebuilt, therefore, to eliminate the first-order dependence of the measured value on the density of the fluid. At the same time, the system was arranged so that part of the apparatus could be used to measure density.

This paper describes the revised viscometer and its use for measurement of the viscosity and density of ethyl chloride, 1-chloropropane, 1-chlorobutane, methyl bromide, ethyl bromide, and 1-bromopropane.

Apparatus

The apparatus (Figure 1) is a steady flow capillary device similar to the one described previously. Volumetric flow in the revised apparatus is established by displacement with mercury at the temperature of the viscosity measurement. The mercury in turn is displaced at 25 °C by the coupled movement of two identical piston syringe pumps driven by a synchronous motor through an adjustable gear train.

With this arrangement it is no longer necessary to know the density of the fluid as a function of temperature in order to calculate the volumetric flow rate through the capillary. The volumetric flow rate can now be established by using well-known density values for mercury.

The mercury displacement technique has the further advantage that heat transfer to mercury-filled lines is rapid. This reduces possible errors in volumetric flow rate resulting from incomplete temperature equilibration of the fluid as it passes from the pump thermostat to the capillary thermostat.

The apparatus can also be used for density measurements. To measure density, the inlet valve to the capillary is closed, and a known volume of fluid is displaced by mercury at constant pressure into an evacuated weighing bottle. The displaced volume is determined by counting turns of the precision lead screw on the mercury pump, and an appropriate correction is made for the temperature difference between the two thermostats.

As in the previous work viscosities were calculated from the modified Poiseuille equation. Thus, the viscosity η is given by

$$\eta = \eta_p - mX \qquad (1)$$

where

$$\eta_p = \pi a^4 \Delta p / (8 Q L_{\text{eff}}) \qquad (2)$$

$$X = \rho Q / (8 L_{\text{eff}}) \qquad (3)$$

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